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STUDY OF THE KINETICS OF CATALYTIC DECOMPOSITION OF HYDRAZINE
VAPORS ON PALLADIUM

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STUDY OF THE KINETICS OF HYDRAZINE
DECOMPOSITION OF HYDRAZINE VAPORS
ON PALLADIUM

A. A. Khomenko and L. O. Apel'baum*

Hydrazine decomposition is described by stoichiometric equations [1]: /1



Catalytic decomposition of hydrazine on the surface of various metals has been studied in a number of publications [2 - 12]. The data obtained in these publications demonstrated that the ratio of decomposition rates of N_2H_4 from equations (1) and (2) depends on the nature of the metal, and on some metals, it also depends on the hydrogen content in the reaction mixture and the reaction temperature. Different hypotheses on the mechanism of the reaction [4, 6, 7 - 13] have been advanced to interpret the obtained data. We studied the decomposition of N_2H_4 on a palladium surface. This was desirable because of the special features of the Pd - H_2 system. There are no corresponding data in the literature. The experiments were conducted in a circulating unit at atmospheric pressure. At 120 - 165° the catalyst used was palladium foil (geometric surface $S = 1140 \text{ cm}^2$), at 220° it was a semipermeable palladium membrane [14].

Hydrazine vapors were fed into the reaction cycle by passing He , H_2 or a mixture of these gases through an evaporator with liquid hydrazine at temperature 80 - 90° and two temperature-controlled

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** Numbers in right margin indicate pagination in original text.

condensers. In the experiments on hydrazine decomposition on the surface of a semipermeable membrane, the catalyst used was a palladium test tube with surface 17 cm^2 sealed into a quartz reaction vessel (50 cm^3 in volume) with the help of a Kovar-molybdenum glass - quartz junction. The inner volume of the palladium test tube was connected to a system containing a gas mercury buret and manometer to supply hydrogen to the reaction side or remove hydrogen from the reaction side. This part of the unit could be filled with hydrogen and pumped out.

The gas mixture emerging from the reaction cycle, after freezing of the formed NH_3 and unreacted N_2H_4 in a liquid nitrogen-cooled trap, entered the gas analyzer to determine the hydrogen content and a foam flow meter. The gas mixture in the gas analyzer was heated to 200° and passed above the external surface of the palladium test tube whose inner volume was connected to a mercury pressure gauge. Hydrogen contained in the analyzed mixture flowed inside of the test tube until the establishment of stationary pressure equal to the partial pressure of H_2 in the mixture; hydrogen pressure was measured by pressure gauge. The N_2 content in the uncondensed gas mixture was determined by the method of gas chromatography. In order to determine the quantity of unreacted hydrazine and the formed ammonia, the hydrazine frozen in the trap and the ammonia were blown out by a helium current into a vial with titered solution of HCl . Titration of individual samples of hydrochloric acid solution by KO and KBrO_3 solutions made it possible to determine the quantity of N_2H_4 and NH_3 .

Experiments were preliminarily conducted on hydrazine decomposition in empty reaction vessels. They showed that under our experimental conditions, decomposition of hydrazine on the walls of the vessel and in the gas phase could be ignored.

The results of the experiments on decomposition of hydrazine are presented in tables 1 and 2. In the tables, Q designates the total volume of gases emerging from the reaction cycle in liters (0.1 atm.)/hour; $P_{\text{N}_2\text{H}_4}$, P_{N_2} , P_{H_2} , P_{NH_3} , P_{He} are the partial

pressures of hydrazine, nitrogen, hydrogen, ammonia and helium in the gas mixture; W_{N_2} and W_{NH_3} are the output of catalyst for nitrogen and ammonia expressed by the volume of the corresponding gas reduced to 0° and 760 mm Hg formed on this quantity of catalyst in one hour. The rates of nitrogen and ammonia formation, r_{N_2} and r_{NH_3} are linked to these quantities by the equalities $W_{N_2} = r_{N_2} \cdot s$ and $W_{NH_3} = r_{NH_3} \cdot s$, where s is the surface of the catalyst. f_{H_2} designates the volatility of hydrogen in palladium measured by stationary pressure of hydrogen on the supply side of the semipermeable membrane [14].

The dependence of W_{N_2} and W_{NH_3} on the composition of the reactive mixture at 140° is presented in table 1. It follows from it that in the mixtures which do not contain added hydrogen, hydrazine decomposition on palladium at 140° occurs predominantly by equation (1). Especially set-up experiments demonstrated that at temperatures 140 - 220° ammonia is not decomposed on palladium, and consequently, hydrogen is formed directly from hydrazine by equation (1). The addition of hydrogen to the initial mixture severely inhibits W_{N_2} . The data presented in table 1 regarding W_{N_2} can be described by the equation:

$$W_{N_2} = K_{N_2} \frac{P_{N_2H_4}^{0.25}}{P_{H_2}^{1.4}}, \quad (3)$$

where K_{N_2} is a constant. The quantities K_{N_2} computed from equation (3) are presented in table 1; within each series of experiments they preserve satisfactory constancy. Deceleration of the reaction by hydrogen to a degree greater than 1 cannot be explained by filling the surface with hydrogen. It should be attributed to reversibility of the intermediate stages of the reaction. The temperature relationship of W_{N_2} is described by an Arrhenius equation with activation energy 21.5 ± 2.5 kcal/mole.

It is difficult to judge the type of dependence of W_{NH_3} at 140° on partial pressures of N_2H_4 and H_2 since with low content of NH_3 in the mixture with hydrazine, the relative error of determining NH_3 was large. This relationship can be approximately represented by an equation of the type /1

$$W_{\text{NH}_3} = K_{\text{NH}_3} P_{\text{N}_2\text{H}_4}^m P_{\text{H}_2}^n \quad (4)$$

where K_{NH_3} is a constant, m and n are exponents ($m = 0.4 - 0.2$; $n = 0.2 - 0$).

Table 2 presents the results obtained from hydrazine decomposition on the surface of a palladium membrane at 220° ; they can be described by the following kinetic equations:

$$W_{\text{H}_2} = K_{\text{H}_2} \frac{P_{\text{NH}_3}^{0.7}}{P_{\text{H}_2}^{0.34}} \quad (5)$$

$$W_{\text{NH}_3} = K_{\text{NH}_3} P_{\text{N}_2\text{H}_4}^{0.6} P_{\text{H}_2}^{0.14} \quad (6)$$

The quantities K_{N_2} and K_{NH_3} computed from equations (5) and (6) are presented in table 2. They are approximately constant within each series of experiments.

It follows from the experimental data obtained in the work at 220° that with specific $P_{\text{N}_2\text{H}_4}$ and P_{H_2} , W_{N_2} and W_{NH_3} have the same value regardless of whether hydrogen is passed through the membrane or is added directly to the original gas mixture. This result does not agree with the hypothesis on the chain mechanism for the reaction with adsorbed atoms of hydrogen as active carriers of the chain [14].

In the absence of a flow of hydrogen through the membrane, stationary hydrogen pressure is on the supply side of the membrane

TABLE 1

RATE OF HYDRAZINE DECOMPOSITION WITH DIFFERENT COMPOSITIONS OF
REACTING MIXTURE. REACTION TEMPERATURE 140°. CATALYST IS PALLADIUM
FOIL: $S_{pd} = 1140 \text{ cm}^2$

(с) Серия и № опыта	Q л/час (d)	Парциальные давления в разгнущей смеси, (е) атм.					\dot{V}_{H_2} см ³ час (f)	\dot{V}_{NH_3} см ³ час (f)	K_{H_2} по уравнению (8) см ³ 0,55 час · атм · 10 ⁻¹ (h)
		$P_{N_2H_4}$	P_{H_2}	P_{H_2O}	P_{NH_3}	P_{H_2O}			
1	2	3	4	5	6	7	8	9	10
2/3	13,46	0,0262	0,0208	0,0405	0,00120	0,911	280,0	16,0	6,9
5	13,51	0,0291	0,0216	0,0422	0,00133	0,906	292,0	18,0	7,0
2	6,50	0,0244	0,0288	0,252	0,00321	0,918	18,7	20,8	6,4
1	6,41	0,0274	0,00126	0,512	0,00477	0,455	8,0	80,6	6,7
4	6,38	0,0246	0,00116	0,515	0,00421	0,455	7,2	26,8	6,6
3/1	13,68	0,0815	0,0271	0,0517	0,00380	0,836	370,0	52,0	4,9
2	14,04	0,0141	0,0137	0,0258	0,00256	0,944	192,5	36,0	4,8
4/1	17,57	0,124	0,0270	0,0538	0,00148	0,794	473,0	26,0	4,4
2	8,82	0,133	0,0382	0,0740	0,00372	0,751	318,0	81,0	4,7
3a)	8,86	0,134	0,0230	0,115	0,00430	0,724	204,0	98,0	5,5
4a)	7,89	0,141	0,00785	0,255	0,00406	0,592	58,0	30,0	4,5

1	2	3	4	5	6	7	8	9	10
5/2a)	14,13	0,0221	0,00477	0,0505	0,00160	0,921	67,5	22,6	2,7
3a)	14,18	0,0425	0,00928	0,0495	0,00198	0,897	131,0	28,0	2,9
1a)	14,10	0,0544	0,0118	0,0490	0,00248	0,882	166,0	35,0	2,9
5a)	14,16	0,0588	0,0115	0,0473	0,00212	0,890	162,0	30,0	2,6
4a, 6b)	10,77	0,113	0,0267	0,0505	0,00426	0,805	237,0	46,0	2,7
6/2	3,04	0,0210	0,00685	0,218	0,00590	0,748	20,8	18,0	6,7
1a)	3,09	0,0496	0,0109	0,228	0,0068	0,710	83,9	21,0	5,3
3a)	3,07	0,0786	0,0140	0,233	0,0065	0,673	43,0	20,0	6,6
5a)	8,05	0,0722	0,0139	0,219	0,0082	0,687	42,5	25,0	7,2
4a)	2,89	0,0865	0,0172	0,250	0,0093	0,637	50,0	23,4	5,7

Key:

- Hydrogen was added to the reaction mixture in the experiment
- Before the experiment, palladium was oxidized and reduced
- Series and number of experiment
- l/h
- Partial pressures in reacting mixture, atm.
- cm³/h
- from equation
- cm³/h x atm.

$\dot{V}_{H_2} \cdot P_{H_2}$ (see table 2). This observation is explained if we assume that the reaction occurs with intermediate formation of hydrogen

atoms which are adsorbed and dissolved in the metal, and their concentration during the reaction is more equilibrium in relation to P_{H_2} [15].

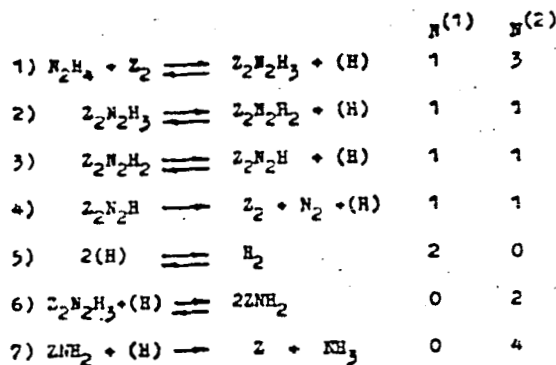
TABLE 2
RATE OF HYDRAZINE DECOMPOSITION WITH DIFFERENT COMPOSITIONS OF REACTING MIXTURE. REACTION TEMPERATURE 220°. CATALYST IS PALLADIUM MEMBRANE; $S_{pd} = 17 \text{ cm}^2$

Сория и № опыта (b)	Q л/ч (c)	Парциальные давления в реагирующей смеси, атм. (d)					f_{H_2} атм. (e)	W_{H_2} см ³ /ч (f)	W_{NH_3} см ³ /ч (f)	K_{N_2} по уравн. (5) (g)		K_{NH_3} по уравн. (6) (g)	
		$P_{N_2H_4}$	P_{N_2}	P_{H_2}	P_{NH_3}	P_{He}							
15/4	4,83	0,129	0,00818	0,00975	0,0132	0,840	0,0145	59,0	64,0	0,4		4,2	
5a)	5,23	0,122	0,00342	0,0085	0,0164	0,760	-	17,8	86,0	3,5		4,2	
8a)	4,72	0,181	0,00291	0,483	0,0216	0,856	-	11,0	102,0	8,4		3,9	
2a)	4,76	0,129	0,00210	0,845	0,0248	-	-	10,0	118,0	3,9		4,1	
1	4,75	0,130	0,00842	0,00968	0,0143	0,838	0,0145	59,8	68,0	8,4		4,4	
16/1	4,76	0,137	0,00708	0,00952	0,0112	0,835	0,0131	53,6	53,8	2,8		8,4	
4	4,88	0,041	0,00885	0,00442	0,0061	0,944	0,0059	18,8	30,0	2,8		4,2	
8	2,22	0,020	0,00495	0,0046	0,0077	0,963	-	11,0	17,1	2,7		3,8	
2	4,65	0,044	0,00410	0,00508	0,0060	0,941	0,0059	18,6	27,7	2,7		8,8	
5	4,99	0,135	0,00786	0,0100	0,0110	0,837	0,0134	56,8	55,0	8,1		3,5	

Key:

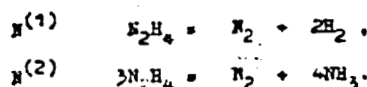
- Hydrogen was added to the reaction mixture in the experiment
- Series and number of experiment
- l/h
- Partial pressures in reacting mixture, atm.
- atm.
- cm³/h
- from equation

The laws indicated above for reaction kinetics could be explained /1/ using the following scheme for their mechanism.



(7)

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Here Z designates the adsorption center on the palladium surface; the area Z_2 contains two of these centers. In scheme (7), $Z_2N_2H_3$ and $Z_2N_2H_2$ designate the chemisorbed particles of N_2H_3 , N_2H_2 and so forth; (H) is the hydrogen atom dissolved in palladium. The stoichiometric numbers are presented on the right of the equations of stages. The columns of stoichiometric numbers determine the base routes of the reaction $N^{(1)}$ and $N^{(2)}$. The summary equation of the route $N^{(1)}$ coincides with equation (1), while route $N^{(2)}$ coincides with equation (2). The presented scheme is similar to the one proposed for the reaction of hydrogenization of ethane [16].

In order to explain the results which refer to 140° , we assume stages 1), 2), 3) and 6) to be equilibrium, and stages 4) and 7) to be irreversible. Considering the surface of the catalyst to be uniform and the coatings of the surface with intermediate forms of dehydrogenization to be small (the percentage of free places on the surface $/Z_2/ = 1$), we obtain from scheme (7) the following kinetic equations:

$$r_{N_2} = k \frac{P_{N_2H_3}}{P_{H_2}}, \quad (8)$$

$$r_{NH_3} = k \frac{P_{N_2H_3}^{0.5} P_{H_2}^{0.5}}{P_{H_2}}. \quad (9)$$

Equation (8) is close to empirical equation (3), while equation (9) agrees qualitatively with equation (4).

In order to explain the kinetic relationships which were obtained at 220° , we assume that at this temperature the equilibrium of stages 2), 3) and 6) is shifted to the right so that these stages become essentially irreversible. In this case, the rate of nitrogen formation r_{N_2} will be determined by the velocity of stage 2), while the velocity of ammonia formation is determined by the velocity of stage 6). In addition it was assumed that at temperature

220° it is impossible to ignore the coating of the surface with chemisorbed particles of N_2H_3 , that is

$$/Z_2/ + /Z_2N_2H_3/ = 1, \quad (10)$$

where $/Z_2N_2H_3/$ is the percentage of the sites on the surface occupied by chemisorbed particles of N_2H_3 . We obtain the following kinetic equations from mechanism (7) with these assumptions:

$$r_{H_2} = k_2 (x_1 x_2^{0.5})^n \left(\frac{P_{N_2H_3}}{P_{H_2}^{0.5}} \right)^n \quad (11)$$

$$r_{N_2H_3} = k_6 \frac{(x_1 x_2^{0.5})^n}{x_3^{0.5}} \left(\frac{P_{N_2H_3}}{P_{H_2}^{0.5}} \right)^n P_{H_2}^{0.5} \quad (12)$$

Kinetic equations (11) and (12) agree satisfactorily with equations (5) and (6) found in experiment if we assume $n = 0.7$. One can come to the conclusion that the scheme proposed above for the mechanism makes it possible to explain the kinetic relationships obtained on palladium. /15

The published data on decomposition of hydrazine on Fe, W, Mo, Cu, Cr and Ir show that on these metals, hydrazine even at low temperatures (60 - 160°) is predominantly decomposed into N_2 and NH_3 . Based on scheme (7), these data can be explained by the fact that stage (5) has very low velocity as compared to stages 6) and 7).

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